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DETERMINATION OF THE OPTIMAL UNIAXIAL PRESSING PRESSURE FOR CERAMIC POWDERS

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The behavior of a mixture of oxide powders during pressing of green bodies is investigated. The entire pressing process can be divided conventionally into three main stages differing by the stability of the ensemble of structural elements of compaction and the possibility of configurational rearrangement or failure of these elements at the critical values of the external forces. A method is proposed for determining the optimal pressure; the method can be classed as an express method because this pressure is determined for green bodies.

Key words: piezoceramic, uniaxial pressing, optimization, pressure, formation of green body, electrophysical characteristics.

In ceramic technology the entire sequence of technological operations occurring before a ceramic material is formed must conform to a unified optimization principle according to which at any given technological stage the process is subject to requirements imposed by the next successive stage and must satisfy these requirements as fully as possible.

The implementation of this principle in the development of a systems approach to the optimization of piezoceramic materials technology makes it possible to preserve freedom of choice of the means for problem solving at individual technological stages. This concerns, first and foremost, the determination of the optimal pressing pressure, which has a predominant influence on the degree of uniformity of the final microstructure of any polycrystalline body which in the process of fabrication necessarily passes through the classical formation operation. In classical ceramic technology uniaxial pressing is such an operation.

Investigations of the microstructure and density of compacts have established that the entire process of pressing a green body can be conventionally divided into three basic stages differing from one another by the stability of the ensemble of structural elements of compaction and the possibility of their configurational rearrangement or breakdown at the critical values of the external forces. It is obvious that the final formation of a green body occurs with the removal of the external pressure, when defects of the microstructure of the sample (microcracks, separation and so forth) form under the action of the residual mechanical stresses.

The dependence of the density of a molded green body on the pressing pressure is presented in Fig. 1 (the dashed lines represent the boundaries between the stages).

The first stage ($0 < p < p_1$) is characterized by the compaction of granulated powder by means of the motion of the structural elements, i.e., granules, under the application of external forces. The motion of the granules continues until the close-packed framework of the molded green body is formed.

At these pressures the green body density changes practically linearly and the granules do not yet fracture. The maximum density attained in this range is determined by the close-packed state of the sample, i.e., the number of granules per unit volume of the sample. By this time the number of point contacts reaches a maximum. At higher external pressures the granules undergo elastic deformation and viscoelastic flow of the granules right up to fracture of individual granules occurs.

The contact area between individual granules increases with increasing external force and reaches a maximum before the granules fracture (Fig. 2*a*). The pressure p_1 corresponding to this moment delimits stage I action. Density increases monotonically in this pressure range. It should be

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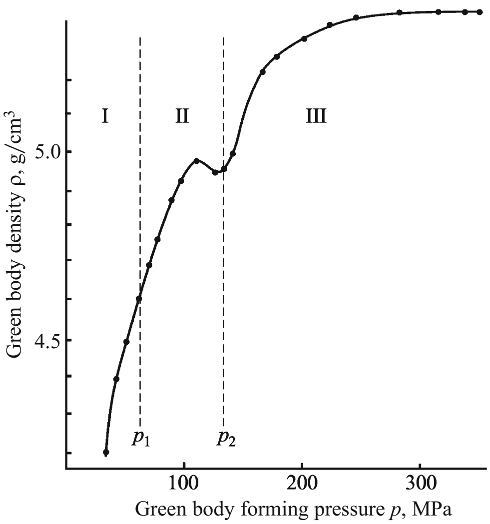

Fig. 1. Green body density ρ versus the pressing pressure p. The dashed lines mark the boundaries between the stages I, II and III.

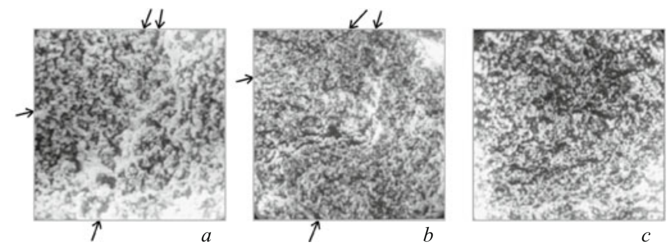

Fig. 2. Microstructure fragments at the stages I (*a*), II (*b*) and III (*c*) of green body formation (fractographic analysis). The arrows indicate the boundaries between the granules.

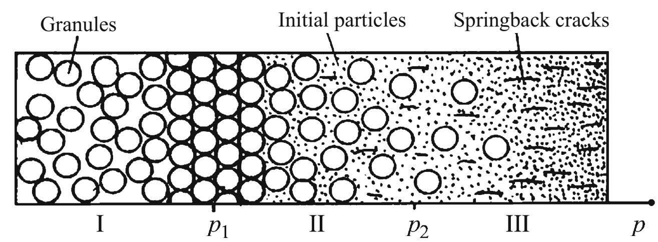

Fig. 3. Schematic distribution of the packing defects at different stages (I, II, III) of the formation of the green body.

noted that the granules remain unfractured during this entire stage.

At the second pressing stage ($p_1 < p < p_2$), together with subsequent compaction of the green body due to the increase in the pressing pressure, individual granules fracture and as a result the density gradually decreases. Qualitative changes associated with a transition of the structural packing elements away from granules (as a result of their fracturing) to the initial particles of the ceramic powder occur in the packing uniformity of the green body, and the packing uniformity of the structural elements decreases (Fig. 2*b*). The onset of fracture of structural elements (granules) and the appearance of a region of loosening is fixed in the photomicrograph. At this stage the density of the green body is determined by the results of the action of these competing processes and deconsolidation can still have a predominant effect on the final density of the sample (see Fig. 1). The second stage is delimited by the pressure p_2 at which the fracturing of the granules is practically completed.

At the third stage ($p > p_2$) the initial particles of the ceramic powder are subject to compaction and after the granules fracture they become the new structural elements. Intense development of local overstresses occurs with increasing pressure; these stresses appear as a result of the reduction of the point contact area between the initial particles of ceramic powder against the background of higher pressing pressures, since the powder particles, having greater elasticity, can concentrate large internal mechanical stresses. This promotes the appearance of springback phenomena, manifested in the mass development of springback microcracks in the sample body after the load is removed (Fig. 2*c*).

At high pressures individual particles undergo further fracturing, and in turn the fragments become new structural packing elements. The character of the microcrack development depends practically completely on the physical-mechanical characteristics of the granular ceramic powder and the technological binder used, which determine the springback after the external pressure is removed. At this stage intense development of macroscopic springback microcracks actually exhausts the possibility of the uniaxial pressing method. Higher pressing pressures can be attained with isostatic cold pressing (ICP), which also is pressure-limited, makes it possible to obtain a green body with a uniform microstructure even at the stage of compaction of the fracturing initial particles and also exhibits a pressure range where the ceramic powder undergoes deconsolidation [1]. The pressure dependence of the green body density is similar to that presented in Fig. 1.

A schematic distribution of the packing defects at all stages of green body formation is presented in Fig. 3.

It should be noted that the green body obtained in the technological chain can have different types of compositional ordering depending on the granulation method used to obtain the powder and the magnitude of the applied pressure. The granulation method, specifically, the method of spray drying (SD) [2] or the method of classical ceramic technology (CT), has the strongest effect on the formation of the green body.

Microstructural analysis shows that the granules comprise hollow spheres in SD and spherical fine-pore formations in CT. In SD the pores between granules in the molded green body will always be smaller than the pores inside the granules themselves. For the CT the pores between granules are always larger those inside granules.

Since the granules obtained by SD show a large variance in the size and character of the porosity in the volume of the

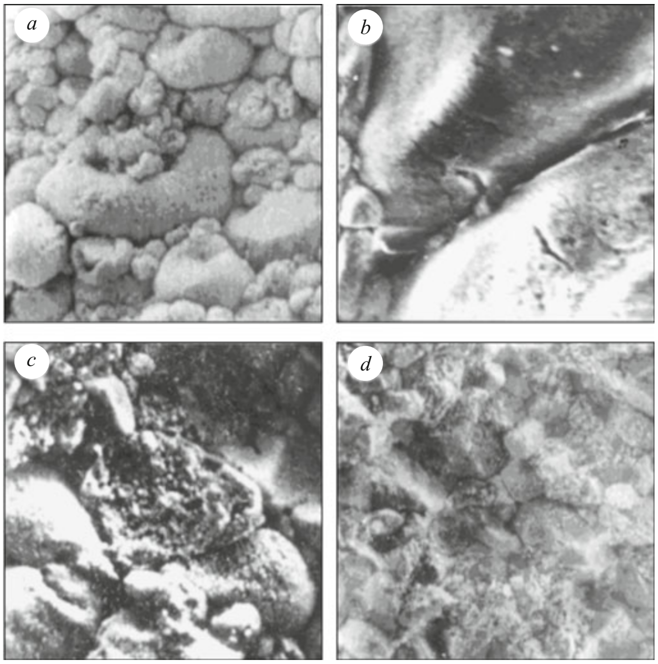

Fig. 4. Fragment of the initial microstructure obtained during the formation of green body for granulation by spray drying, fractographic analysis: *a*) $p = p_{S_{max}}$; *b*) $p > p_{S_{max}}$; *c*) $p \gg p_{S_{max}}$; *d*) $p = p_1$.

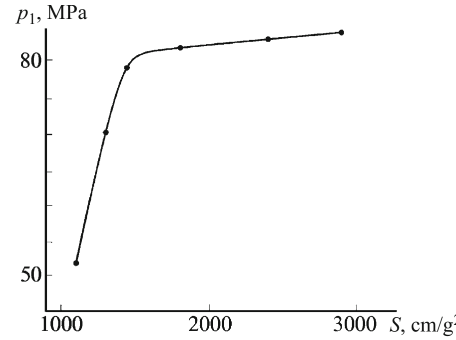

Fig. 5. Optimal pressing pressure p_1 for the green body versus the specific surface area S of the ceramic powder.

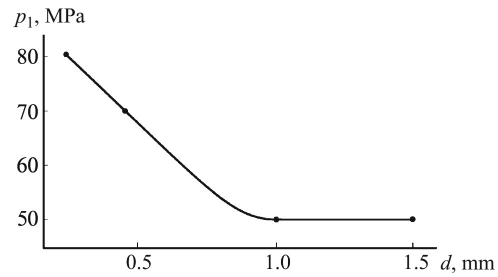

Fig. 6. Optimal pressing pressure p_1 for the green body versus the powder granule diameter d.

green body, the maximum packing uniformity observed in CT is not observed when the maximum contact area S_{max} between granules is reached (Fig. 4*a*). The granules fracture with increasing pressing pressure, and this process starts with larger and softer granules. The 'fragments' of the fractured granules become comparable in size to the small granules, which increases the uniformity of the green body as a whole (Fig. 4*b* and *c*). In the case of SD the maximum uniformity of the green body is a compromise between the size uniformity of the granules and the distribution uniformity of the intergranular porosity in the interior of the green body (Fig. 4*d*). As the molding pressure increases with incomplete granule fracturing springback microcracks, whose distribution is determined by the residual mechanical stresses on removal of the external pressure, start to appear in the body.

In this connection it must be said that if the SD method is used for granulation of the initial ceramic powder and the initial microstructure of the green body has maximum uniformity, the applied pressure must be higher than in the CT method. As the dispersity of the synthesized powder increases (the conditions of granulation remaining unchanged) the porosity of the granules and, in consequence, p_1 increase. In addition, this dependence is strongest for larger particles (with smaller specific surface area) (Fig. 5).

Since the strength of the starting granules depends strongly on their size, p_1 also depends on p_1 (Fig. 6). Evidently, p_1 decreases with increasing granule size. But the presence of granules of different sizes in the interior of the green body also results in lower p_1, which is determined by the size of the largest granules.

Analysis of the results of these studies showed that the pressure p_1 corresponding to the most uniform microstructure of the green body depends strongly on the past history of the molding powder, while the uniformity of the microstructure itself is determined by the pressure at which the process of molding the green body was interrupted. Studies of the behavior of the compaction of the green body by uniaxial molding show that the choice of the molding pressure $p = p_1$ in the process of molding the green body takes a special place, since the most uniform packing (initial microstructure) of its structural elements obtains precisely at this pressure.

Regarding the molded green body as a three-phase composite consisting of crystalline (synthesized powder), polymer (binder) and gas (air) phases, not only the nature of the formation of the type of compositional ordering found in the interior of the body but also that of the final microstructure becomes understandable.

This is associated with the fact that a complex system of micro nonuniformities and residual mechanical stresses, which directly affects the sintering process and, in consequence, the nonuniformity of the final microstructure of the polycrystalline material, is established during the molding of the green body. An interruption of the molding process at different stages (different values of p) establishes in the interior of the green body a definite system of stresses and micro nonuniformities, which, in turn, predetermine the flow of the sintering process as well as the uniformity of the final microstructure.

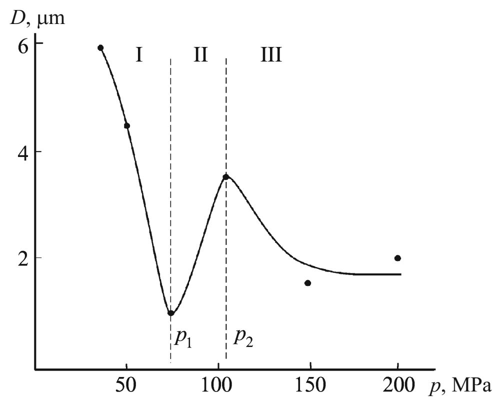

Fig. 7. Average pore diameter D in sintered ceramic samples versus the pressing pressure p for a pre-sintered body.

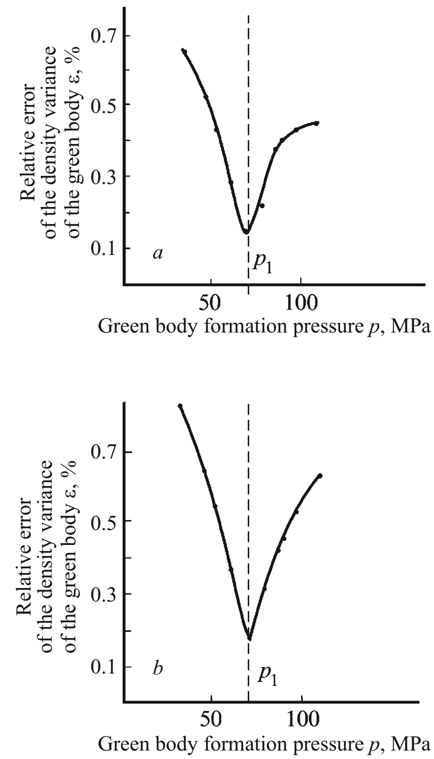

Fig. 8. Density variance for a pre-sintered body (a) and sintered ceramic (b) versus the pressing pressure for the green body.

This is due to the fact that the scale of each type of residual mechanical stress makes its own contribution to the formation of the final microstructure. For example, stress of the second kind will promote earlier sintering of grains, stress of the first kind will promote the formation of springback cracks and stress of the first kind close to that the second kind will promote the formation of large pores in the interior of the sintered sample. The effect of the technological factors on the formation of the final microstructure is seen at practically all stages of the ceramic technology.

A comparative analysis of the starting and final microstructures of green bodies whose formation process was interrupted at different stages of formation established that the pore size and the presence of loosening and microcracks in the packing of the structural elements arising during the formation of the green body retain their position in the succession of states at the sintering stage also.

The investigations showed that as a rule a change of the temperature–time characteristics of sintering does not result in the complete elimination of the effect of the distribution of the defects indicated, either with respect to sizes or in the interior of the green body itself. This is associated with the fact that the sections with finer porosity (just as the locations of local springback) start to sinter at lower temperatures, thereby promoting anisotropy of the sintering process and the appearance of additional defects in the sintered green body.

It should be noted that at the initial stage of the formation of the green body, when intergranular pores determine the total porosity, large pores approximately uniformly distributed in the entire volume of the sample are observed in the ceramic. As the pressing pressure increases the size D of these pores gradually decreases (Fig. 7). In the place of these pores, at large molding pressures there appear new, nonuniformly distributed, elongated pores, which apparently are a consequence of the fracture of the granules at the second stage of the molding process. At the third stage of the molding process the size of these pores gradually decreases, even though springback cracks appear. The samples obtained at this stage of molding exhibit regions of microstructure with anomalously large grains.

These results not only attest to the very fact that the residual mechanical stresses affect the formation of the microstructure but they also confirm that the mechanisms of such influence, which depend on the type of residual stresses in the interior of the green body, are different.

In summary, the properties of ceramic materials can be determined by the following chain: starting material – technology – microstructure – properties. For pressing pressure $p > p_1$ the variance of the parameters of a ceramic material is determined by the density nonuniformity of the green body formed at the initial stage of compaction. For $p \gg p_1$ the density variance depends on the character of the fracture of the initial granules and the probability of the nucleation of springback cracks in a particular ceramic powder at the given pressure. The pressure p_1 depends completely on the individual features of the particular molding powder and its production history.

To confirm the theoretical and experimental results the effect of the apparatus factor on the optimal pressure p_{op} under factory conditions was studied for the formation of long serial green bodies for the fabrication of piezoelectric ceramic of the type TSTS in 5000 piece batches. Figure 8 displays the variance in the density of molded (Fig. 8a) and sintered (Fig. 8b) samples versus the pressing pressure of the green bodies. Evidently, the minima of the density variance

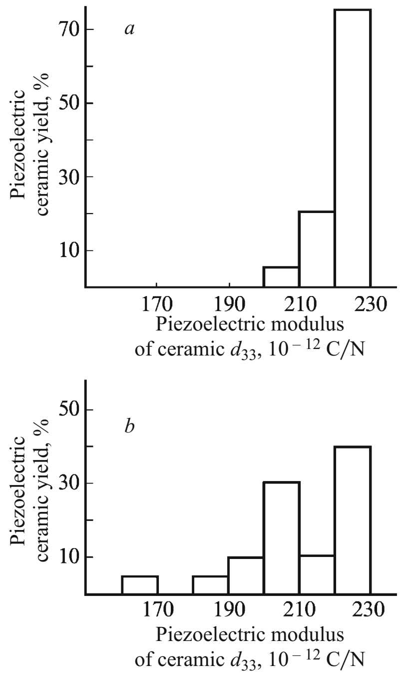

Fig. 9. Effect of the microstructure uniformity of the green body on the variance of the electrophysical parameters of TSTS type piezoceramic. The body was pressed at $p = p_1$ (*a*) and $p \neq p_1$ (*b*).

coincide with one another and correspond to samples whose molding process was interrupted at pressure p_1. The values of the piezoelectric modulus d_{33} in the histograms were obtained at $p = p_1$ (Fig. 9*a*) and at $p \neq p_1$ (Fig. 9*b*). The piezoelectric modulus $d_{33} = (229.15 \pm 3.78) \times 10^{-12}$ C/N (variance $\cong 1.6\%$) in the first case and $d_{33} = (212.12 \pm 11.22) \times 10^{-12}$ C/N (variance $\cong 5.3\%$) in the second case. It is evident that the minimum variance of the piezoelectric modulus corresponds to the maximum uniformity of the initial microstructure of the green bodies obtained at $p = p_1$. The behavior found extends to all performance characteristics of the piezoceramic, including the stability of the resonance frequencies over all vibrational modes, which depend directly on the stability of the uniformity of the green body.

Therefore, if the optimization criterion for the pressing pressure is taken to be the conservation of the useful electrophysical properties of the piezoceramic with minimum variance, then $p_{op} = p_1$ must be taken as the optimal pressure [3].

Indeed, if the state of the green body corresponding to this pressure is evaluated from the standpoint of the next stage of synthesis, then it is closest to ‘ideal’ precisely by the end of the first stage. The green body by this time is characterized by the following:

– maximum packing uniformity of the structural elements (granules);

– most uniformly stressed state as a whole, since it is determined by the elastic interaction of the granules, inasmuch they have not yet begun to fracture;

– absence of (or, at least, minimum number of) points of local springback, characteristic for higher pressures, when the role of the structural element of the green body passes from the granule (after it fractures) to the initial particle of the ceramic powder.

It should be noted that the apparatus error of the pressing equipment has a special influence on the pressing pressure. The degree of this effect is determined on the one hand by the probability of the pressing force generated by the operator of the manual press or automatic press being repeating and on the other hand by the state of the mold press, especially a multiposition and long machine. This is associated with the fact that small deviations of the dimensions of the pocket of the mold press induce significant changes in the variance of the parameters characterizing the molded green body as a whole.

Since it is unlikely that in actual ceramic production identical properties will obtained in different technological batches of the molding powder, it becomes understandable that the pressure p_{op} must be determined for each technological batch of the material and that it is incorrect to use a single value for it.

Systems analysis of the studies enabled the following:

– formulation of the concept and implementation of a computer model adequately predicting the process of formation of the synthesized powders of oxide materials taking account of the factors affecting it;

– development of a method for determining the optimal molding pressure.

The method of determining the optimal pressure can be classed as an express method because the pressure p_{op} is determined for green bodies. Since the principle of searching for the pressing pressure that minimizes this variance is incorporated in the method itself, control sintering is not necessary to obtain more accurate values of the variance of the electrophysical characteristics of the final product.

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